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Triple molybdates one-, one - and three(two)valence metals

the review summarizes experimental data on the phase formation, structure and properties of new complex oxide compounds group – triple molybdates containing tetrahedral molybdate ion, two different singly charged cation, together with tri- or divalent cation. The several structural families of these compounds were distinguished and it shown that many of them are of interest as luminescent, laser, ion-conducting or nonlinear optical materials.

Keywords: triple molybdates, one-, two - and trivalent metals, phase formation, structure, functional properties.

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The molybdates and tungstates are among the most popular objects of inorganic chemistry, crystal chemistry and solid state chemistry, as well as a base for developing of functional materials for various purposes, which maintains a constant interest in these compounds and explains a significant number of publications on this subject.

In 1960-80 the focus of the scientists was double molybdates and tungstates phases with the general formula $A_xB_y(XO_4)_z$, on the basis of which laser, ferroelectric, scintillation, nonlinear optical and other materials were later developed [1-5]. The main contribution to the formation of this group of compounds and their comprehensive study was made of the Russian scientific school: professor Kovba L. M., professor Trunov V. K. (Moscow state University named M. V. Lomonosov), professor Zhukovsky V. M, professor Tkachenko E. V. (Ural state University named A. M. Gorky, Sverdlovsk), corresponding member of Academy of Sciences of USSR Mokhosoev M. V. (Donetsk state University; Buryat Institute of natural Sciences, Sibiriyan Brunch of Academy of Sciences USSR, Ulan-Ude), professor Mayer A. A (Moscow chemical-technological Institute named D. I. Mendeleev), professor Golub A. M. (Kiev state University), candidate of physico-mathematical sciences Klevtsova P. V., candidate of physico-mathematical sciences Klevtsova R. F. (Institute of inorganic chemistry of Sibiriyan Brunch of Academy of Sciences USSR, Novosibirsk) and etc.

In the last two decades there has been a shifting of the centre gravity of studies from double molybdates and tungstates on triple molybdates. To date, this group of compounds has more than 550 individuals and is the fastest growing of complex oxide phases containing tetrahedral anion and cation. The large part of triple molybdates is prepared and is characterized by the employees of the Baikal Institute of nature management SB RAS (Ulan-Ude) and the Institute of inorganic chemistry named A. V. Nikolaev SB RAS (Novosibirsk). A brief overview of the different types of triple molybdates, different combinations of the charges of their constituent cations is earlier presented in [6]. The aim of this work is a detailed consideration of the phase formation, structure and properties of triple molybdates, containing two different singly mono-charged cation along with triple-charged (type 1-1-3) or doubly charged (type 1-1-2) cation.

Triple molybdates of the type 1-1-3

The first systematic searching researches of triple molybdates of one-, one-, and trivalent metals were conducted for lithium-containing systems Li_2MoO_4–M_2MoO_4–$R_2(MoO_4)_3$ (M = K–Cs, Tl, Ag, R = Bi, *Ln*, Y, In, Sc, Fe, Ga, Cr, Al). Their result was the identification, synthesis and characterization of about 40 compounds of compositions $LiMR_2(MoO_4)_4$, $LiM_2R(MoO_4)_3$, $Li_2M_3R(MoO_4)_4$, $LiM_4R(MoO_4)_4$, $Li_2MR(MoO_4)_3$ which initiated the formation of an extensive group of triple molybdates of the type 1-1-3. The typical variants of systems triangulation in which these phases are formed are represented in Fig. 1. The belonging of the considered compounds to eight structural types is set, for representatives of five of whom crystals were obtained and the crystal structures are determined

Triple molybdates of the most numerous isostructural series of compounds of the composition $LiMR_2(MoO_4)_4$ are formed with the bismuth and lanthanides on some quasi-binary sections of $LiR(MoO_4)_2$–$MR(MoO_4)_2$ of systems Li_2MoO_4–M_2MoO_4–$R_2(MoO_4)_3$ (M = K, Rb, Tl). The domains of existence of these

phases in a series of REE vary significantly and with increasing size of singly charged cations move in the direction to the light lanthanides (Fig. 2).

The analysis of experimental data allows to draw a conclusion about the decisive influence of dimensional factor on the possibility of the formation of monoclinic triple molybdates of this family: $LiMLn_2(MoO_4)_4$ are formed, if the difference in sizes of ions of large singly charged cation and rare earth element lies in the interval. 0.48 Å ≤ $r(M^+) - r(Ln^{3+})$ ≤ 0.60 Å.

At lower values of Δr in the cut of $LiLn(MoO_4)_2$–$MLn(MoO_4)_2$ there is the formation of solid solutions. When $\Delta r >$ 0.60 Å the consider phase is either not formed or its formation is so complicated that the connection cannot be allocated in single-phase condition using conventional methods of solid-phase synthesis [11].

Within the prescribed time interval the isothermally and isostructural copper compounds $CuKLn_2(MoO_4)_4$ with Gd, Tb, Ho are prepared and characterized in [12, 13] are stacked. The closeness of $r(Cu^+)$ and $r(Li^+)$ with a high degree of probability allows to predict a significant expansion of the triple molybdates $M'M''R_2(MoO_4)_4$ due to containing Cu(I) phases of this type with K, Tl, Rb, and those of trivalent elements, the difference in dimensions which will satisfy the proposed criterion.

The structure of triple molybdates $LiMR_2(MoO_4)_4$ is defined by the exam-

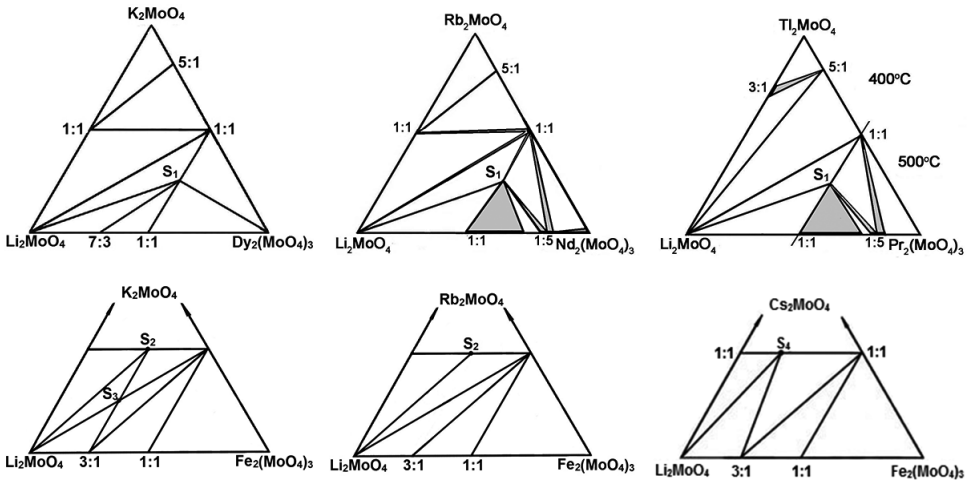

Fig. 1. Subsolidus structure of some systems Li_2MoO_4–M_2MoO_4–$R_2(MoO_4)_3$ [7–10]: S_1 – $LiMR_2(MoO_4)_4$; S_2 – $LiM_2R(MoO_4)_3$; S_3 – $Li_2MR(MoO_4)_3$; S_4 – $Li_2M_3R(MoO_4)_4$.Region $LiMMoO_4$–M_2MoO_4–$MFe(MoO_4)_2$ систем Li_2MoO_4–M_2MoO_4–$Fe_2(MoO_4)_3$ (M = K, Rb, Cs) is not a quasi-threefold.

M \ *Ln*	La	Ce, Pr	Nd	Sm, Eu	Gd–Lu, Y
K			■	■	■
Tl		■	■	■	
Rb	■	■	■	■	

Fig. 2. The domains of existence of triple molybdates $LiMLn_2(MoO_4)_4$ (shaded)

ple $LiRbBi_2(MoO_4)_4$, the only compound of this family which congruently melting [14]. Other compounds $LiMR_2(MoO_4)_4$ decompose in the solid phase at the corresponding double molybdates [7, 15] and their structure (for example $LiMNd_2(MoO_4)_4$, M = K, Tl, Rb) was refined by the Rietveld method for powder data [16]. The structures $LiMR_2(MoO_4)_4$ are close to the structure of triple molybdates $Li_3Ba_2Ln_3(MoO_4)_8$ [17] and are derived from the structural type $BaNd_2(MoO_4)_4$ [18]. A characteristic features of structures $LiMR_2(MoO_4)_4$ are the laced layers of the RO_8 polyhedron and connected to them through common vertices MoO_4-tetrahedra. The neighbouring layers are interconnected by octahedra and LiO_6 polyhedra MO10 (Fig. 3).

The presence in compounds $LiMR_2(MoO_4)_4$ ions Li^+, filling the interstitial voids of the structural type $BaNd_2(MoO_4)_4$ suggests that they have lithium ionic conductivity. The results [19, 20] indicate the possibility of using these triple molybdates as sensitive elements of sensors of sensor systems for operational environmental monitoring. Spectral-luminescent characteristics $LiMLn_2(MoO_4)_4$: Eu^{3+}(Nd^{3+}) give the basis to speak about the possibility of the application of triple molybdates of this family to create luminophors with high contrast colors, as well as active media of lasers [8, 21]. The data obtained in [22] show the availability of using $LiKGd_2(MoO_4)_4$: in the capacity of: Eu^{3+} is as a red phosphor for WLED.

As in the previous case, the possibility of formation of other isostructural series of triple molybdates $Li_2M_3R(MoO_4)_4$ (MR = CsFe, CsGa, RbGa, CsAl, RbAl, TlAl) is largely determined by a dimensional factor: compounds are formed by small cations Fe^{3+}, Ga^{3+}, Al^{3+} with tetrahedral coordination and quite major ions Tl^+, Rb^+ and Cs^+. The absence $Li_2M_3Cr(MoO_4)_4$ is apparently due to the high preference of Cr^{3+} in octahedral coordination. These tetragonal compounds have a frame structure and are ordered derivatives of the cubic $Cs_6Zn_5(MoO_4)_8$ [23, 24]. With the increasing of size of R^{3+}, the region of existence of these phases shifts towards larger singly charged cations M^+, which can be explained by the compliance of the sizes of the tetrahedral framework and the size of the extra framework cation. Obviously with namely dimensional discrepancy the crystallization $Li_2K_3Al(MoO_4)_4$ is bound in a different structural type [10].

It is shown that $LiK_2In(MoO_4)_3$, $LiRb_2Fe(MoO_4)_3$, $LiCs_4Al(MoO_4)_4$ and $LiCs_4Al(MoO_4)_4$ form new structural types that have not other members (table 1). Get fit for x-ray crystallographic

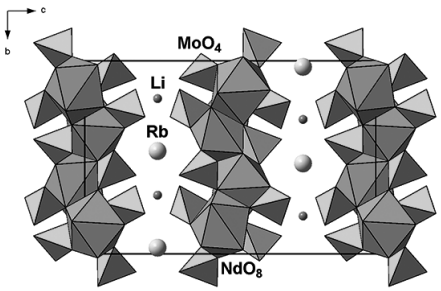

Fig. 3. Projection patterns $LiRbNd_2(MoO_4)_4$ along the axis *a*

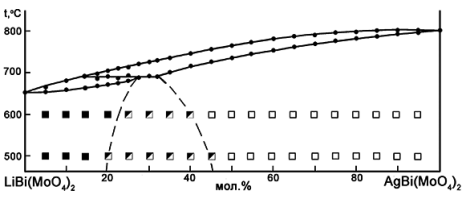

Fig. 4. *T*–x-diagram of a cut $LiBi(MoO_4)_2$–$AgBi(MoO_4)_2$ [29]

studies single crystals of $LiK_2Fe(MoO_4)_3$, $Li_2KFe(MoO_4)_3$ and $Li_2K_3Al(MoO_4)_4$ or to find structural prototypes of these compounds have not yet succeeded.

In none of the systems Li_2MoO_4–Ag_2MoO_4–$R_2(MoO_4)_3$ triple molybdates are not found [28-30]. The incisions $LiR(MoO_4)_2$–$AgR(MoO_4)_2$ in the bismuth- and lanthanoid-containing systems are characterized by the formation of extended boundary solid solutions (Fig. 4).

Made in recent years the researches of systems M_2MoO_4–Cs_2MoO_4–$R_2(MoO_4)_3$ (M = Na, Ag) allowed significantly to fill the group of triple molybdates of one-, one- and trivalent metals due to the sodium and silver-containing phases. The compositions and the fields of the existence of thus obtained compounds are shown in table. 2, the data of the RSA of the obtained single crystals are presented in table. 3.

Studied sodium compounds have, as a rule, difficult structures and frame structures (Fig. 5, 6), different in structure from the triple molybdates formed in the systems Li_2MoO_4–M_2MoO_4–$R_2(MoO_4)_3$ (M = K–Cs, Tl). In the structures of the sodium-containing triple molybdates MoO_4-tetrahedra and RO_6-octahedra are present and sodium has an octahedral or trigonal-prismatic coordination or generates polyhedra with lower CN. In these structures the Na^+ and R^{3+} quite often jointly occupy one crystallographic position; along with them there are positions which partially filled with sodium cations that leads to the deviation of composition from stoichiometry. The phases of variable composition are widely distributed among the complex (double and triple) sodium molybdates [33, 34], due to the proximity of sizes of ions Na^+ and A^{2+} or R^{3+}.

According to the data of RSA, all triple molybdates found in the systems Ag_2MoO_4–Cs_2MoO_4–$R_2(MoO_4)_3$ are isoformular to sodium analogs and are built on the same structural basis [32].

Table 1

Data RSA single crystals $LiK_2In(MoO_4)_3$, $LiRb_2Fe(MoO_4)_3$ and $LiCs_4Al(MoO_4)_4$ [25–27]

Compound	Pr. gr.; Z	*a*, Å	*b*, Å	*c*, Å	β, °	*R*, %
$LiK_2In(MoO_4)_3$	$P2_1$; 2	7.0087(2)	9.2269(3)	10.1289(3)	107.401(1)	22.80
$LiRb_2Fe(MoO_4)_3$	*Pnma*; 4	24.3956(6)	5.8306(1)	8.4368(2)	–	2.11
$LiCs_4Al(MoO_4)_4$	*P*2; 2	15.940(3)	8.266(2)	8.319(2)	105.13(3)	2.85

Table 2

Triple molybdates in systems M_2MoO_4–Cs_2MoO_4–$R_2(MoO_4)_3$
(M = Na, R = Bi, *Ln*, In, Sc, Fe; M = Ag, R = Bi, *Ln*, In, Sc) [31, 32]

	M = Na							Phase	M = Ag				
	Bi	Tm	Yb	Lu	In	Sc	Fe		Bi	Yb	Lu	In	Sc
S_1	*	*						$M_{13-3x}Cs_{11}R_{2+x}(MoO_4)_{15}$					
S_2			*					$M_5Cs_7R_2(MoO_4)_9$					
S_3	*							$MCs_2R(MoO_4)_3$	◆				
S_4					*в/т н/т			$M_3Cs_3R_2(MoO_4)_6$					
S_5					*	*	*	$M_{25}Cs_8R_5(MoO_4)_{24}$					

fields of compounds, based on common structural basis, equally shaded

* – the resulting crystals and structure was determined on single crystal data by method RSA;

◆ – the resulting crystals and settings of cells were determined on single crystal data.

Table 3

Data RSA of single crystals of triple molybdates of sodium, cesium and trivalent metals [31]

	Compound	Pr. gr.; Z	Lattice parameters	R
S_1	$Na_{7.23}Cs_{11}Tm_{3.92}(MoO_4)_{15}$	$P6_3/mcm$; 2	a = 10.5849(1), c = 37.4867(6) Å	0.029
	$Na_{7.72}Cs_{11}Bi_{3.76}(MoO_4)_{15}$	$P6_3/mcm$; 2	a = 10.5507(1), c = 37.6640(1) Å	0.038
S_2	$Na_5Cs_7Yb_2(MoO_4)_9$	$R32$; 3	a = 10.5107(2), c = 36.358(7) Å	0.035
S_3	$NaCs_2Bi(MoO_4)_3$	$R3c$; 12	a = 10.6435(2), c = 40.9524(7) Å	0.020
S_4	в/т-$Na_3Cs_3In_2(MoO_4)_6$	$R\bar{3}$; 12	a = 17.5753(2), c = 29.4333(3) Å	0.032
S_5	$Na_{25}Cs_8In_5(MoO_4)_{24}$	$P2_1/c$; 4	a = 12.6392(2), b = 21.4601(4), c = 14.0313(3) Å, β = 90.017(1)°	0.030
	$Na_{25}Cs_8Sc_5(MoO_4)_{24}$	$P2_12_12_1$; 2	a = 28.6452(6), b = 14.0043(3), c = 12.6482(2) Å	0.072
	$Na_{25}Cs_8Fe_5(MoO_4)_{24}$	$P\bar{1}$; 2	a = 12.5814(5),b = 13.8989(5), c = 28.4386(9) Å, α = 90.108(2), β = 90.064(2), γ = 90.020(2)°	0.044

In practical terms, triple molybdates $Na_{25}Cs_8R_5(MoO_4)_{24}$ are the most interesting which the closely related structures are solved by single crystal data in the framework of pr. gr. $P2_1/c$ (In), $P2_12_12_1$ (Sc), $P\bar{1}$ (Fe) [38, 39]. The Mo atoms in all three structures are coordinated tetrahedral, trivalent metal is octahedral, all or some of them occupy their positions together with the atoms of sodium. The remaining Na atoms have rather distorted oxygen coordination (CN = 5 and 6); the atoms of cesium are CN = 9-10 (In), 11 (Sc), 10-12 (Fe); some positions of the sodium cations may be partially settled. In all structures it is possible to allocate polyhedral layers which formed by pairs of articulated along edges of the octahedra (R, Na)O_6 and (R, Na)O_6 (or RO_6) that are connected by vertices with bridging MoO_4-tetrahedra (Fig. 6, *a–c*). The layers contact bridging MoO_4-tetrahedra in the

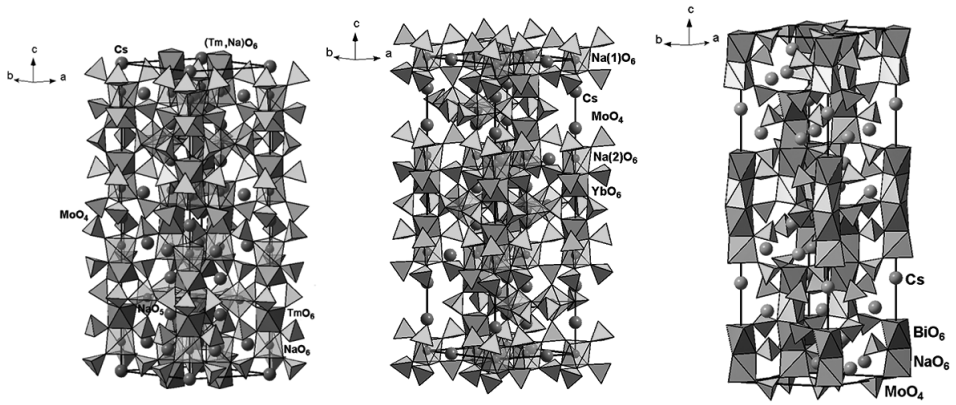

Fig. 5. Structures $Na_{7.23}Cs_{11}Tm_{3.92}(MoO_4)_{15}$ (*a*), $Na_5Cs_7Yb_2(MoO_4)_9$ (*b*), $NaCs_2Bi(MoO_4)_3$ (c) [35–37]

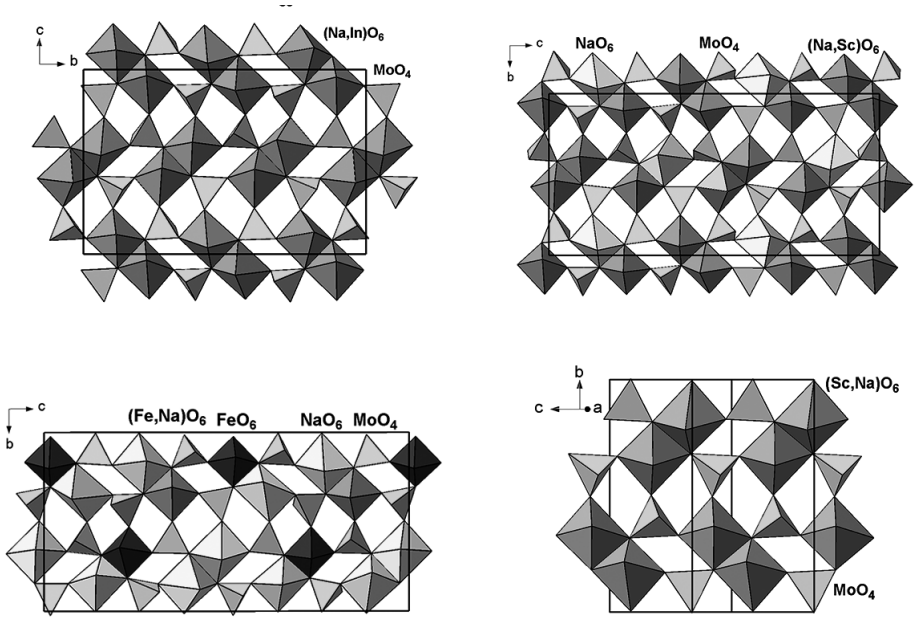

Fig. 6. Polyhedral fragments (layers) in the structures $Na_{25}Cs_8In_5(MoO_4)_{24}$ (*a*), $Na_{25}Cs_8Sc_5(MoO_4)_{24}$ (*b*), $Na_{25}Cs_8Fe_5(MoO_4)_{24}$ (*c*), $Na_5Sc(MoO_4)_4$ (*d*) [38]

three-dimensional skeleton the voids of which are cations Cs^+ and Na^+. In all cases the structure of the layers goes back to the polyhedral layer of patterns $Na_5Sc(MoO_4)_4$ (Fig. 6, d), related to the type alluaudite (Na, Ca)(Fe, Mn, Mg) $_3(PO_4)_3$ [40]. The rhombic or pseudorhombic metric of cells of triple molybdates occurs due to some mutual shift of the layers in comparison with monoclinic $Na_5Sc(MoO_4)_4$ and alluaudite (pr. gr. *C*2/*c*), which may be due to the presence of cesium cations between the layers. Structural features of this group of triple molybdates suggests that this is not the kind of structural type of alluaudite and a separate, let closely related structural family.

The study of alluaudite-like ion-conductive properties of triple molybdates showed that these compounds undergo reversible phase transitions of type I, followed by an abrupt increase of conductivity. Above the temperatures of phase transitions, the electrical conductivity reaches values of 10^{-2}–10^{-3} sm/Sm, which gives an opportunity to consider $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = In, Sc, Fe) as the promising objects for the development of new materials with high ionic conductivity [38, 39].

The structural features of the other described above triple molybdates also allow to expect the existence of them increased the sodium (silver)-ionic conductivity and improve their conductive characteristics that apparently it is possible to achieve by suitable heterovalent substitutions with replacing part of the sodium (silver) or other cation in the structure on more high strength field and education vacancies.

Triple molybdates of type 1-1-2

Among triple salt systems M'_2MoO_4–M''_2MoO_4–$AMoO_4$ to date, the most studied systems are that consist of lithium molybdate, heavy alkali elements (K, Rb, Cs) and Mg, Mn, Co, Ni, Co, Zn, Cd, Ca, Sr, Ba, Pb. Most of these systems are not phase-forming, the solid solutions are formed in some of them on the basis of double molybdates. One triple molybdate was found in the six systems; their characteristics are presented in table. 4.

In the triple systems Li_2MoO_4–K_2MoO_4–$AMoO_4$ (A = Mg, Mn, Co) in quasi-binary sections $Li_2A_2(MoO_4)_3$–$K_2A_2(MoO_4)_3$ (Fig. 7) the rhombohedral triple molybdates $K_{3+x}Li_{1-x}A_4(MoO_4)_6$ ($0 \le x \le 0.3$) are revealed [42, 43]. They crystallized in the structural type II-$Na_3Fe_2(AsO_4)_3$ [49], in which the cations are distributed as follows: $(Na_5\square)^{IX}(M1)^{VI}(M2)^{VI}(M3)_3{}^{VI}(AsO_4)_6$ = $(Na_5\square)(Na)(Fe^{3+})(Fe^{3+})_3(AsO_4)_6$ (here the Roman numerals denote the CN of the cations in the positions M1, M2 and M3). In the structures of the triple molybdates cations Li, A^{2+} and K^+ are placed at the positions M1, M2 and M3 (Fig. 8), and the main part of the potassium is in a position with CN = 9, busy half due to short contacts C–C. The presence of potassium in the same position with the cations Mg^{2+}, Mn^{2+}, Co^{2+}, Li^+ is rare case for crystal chemistry. Found on the structural data the compositions of the crystals are confirmed by good convergence of the local balance of valence efforts. The basis of all structures are three dimensional frames from octahedra around M1, M2 and M3 and tetrahedra

Table 4

Crystallographic and thermal properties of triple molybdates of the type 1-1-2 [41–48]

Compound	Pr. gr.; Z	The unit cell parameters				T_{melt}, °C
		a, Å	*b*, Å	*c*, Å	β, °	
$K_{3.11}Li_{0.89}Mg_4(MoO_4)_6$	$R\bar{3}c$; 6	14.3541(2)	–	19.7338(4)	–	730*
$K_{3.07}Li_{0.93}Mn_4(MoO_4)_6$	$R\bar{3}c$; 6	14.5896(3)	–	19.9773(8)	–	720
$K_{3.14}Li_{0.86}Mn_4(MoO_4)_6$	$R\bar{3}c$; 6	14.607(2)	–	19.992(4)	–	–
$K_{3.30}Li_{0.70}Co_4(MoO_4)_6$	$R\bar{3}c$; 6	14.4391(3)	–	19.891(1)	–	710*
$K_3NaNi_4(MoO_4)_6$	$R\bar{3}c$; 6	14.2790(2)	–	19.7589(4)	–	750
$K_3NaMg_4(MoO_4)_6$	$R\bar{3}c$; 6	14.4528(2)	–	19.8894(3)	–	720
$K_3NaCo_4(MoO_4)_6$	$R\bar{3}c$; 6	14.4638(1)	–	19.8369(3)	–	530*
$Rb_3LiZn_2(MoO_4)_4$	$I\bar{4}3d$; 4	11.902(1)	–	–	–	580
$Cs_3LiCo_2(MoO_4)_4$	$I\bar{4}3d$; 4	12.2239(2)	–	–	–	740**
$Cs_3LiZn_2(MoO_4)_4$	$I\bar{4}3d$; 4	12.2100(1)	–	–	–	690
$Cs_3NaZn_2(MoO_4)_4$	$I\bar{4}3d$; 4	12.3134(1)	–	–	–	510
$Cs_3AgZn_2(MoO_4)_4$	$I\bar{4}3d$; 4	12.3049(2)	–	–	–	530
$CsNa_5Mn_3(MoO_4)_6$	$C2/c$; 2	13.3659(3)	13.6897(3)	7.1692(2)	112.727(1)	701
$Cs_4Na_{10}Mn_5(MoO_4)_{12}$	$P2_1/c$; 4	13.8597(3)	12.5719(2)	28.4209(3)	90.097(1)	576
$CsNa_5Co_3(MoO_4)_6$	$C2/c$; 2	13.0917(8)	13.5443(8)	7.1217(4)	112.331(2)	615
$Cs_4Na_{10}Co_5(MoO_4)_{12}$	$Pbca$; 4	13.6572(3)	12.5063(3)	27.9898(5)	–	–
$CsNa_5Ni_3(MoO_4)_6$	$C2/c$; 2	13.212(3)	12.458(3)	7.120(1)	112.245(3)	636

* The compound decomposes in the solid phase of the double molybdates.

** Compound decomposes in the solid phase at $Cs_2Co_2(MoO_4)_3$ и $CsLiMoO_4$.

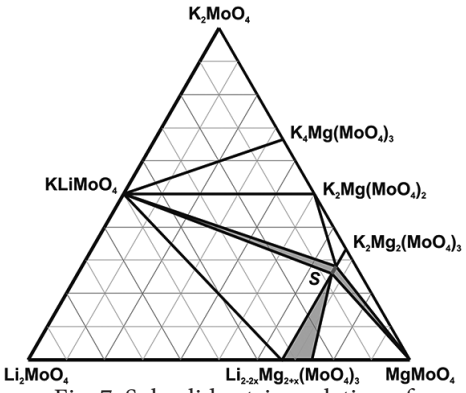

Fig. 7. Subsolidus triangulation of Li_2MoO_4–K_2MoO_4– $MgMoO_4$ at 550 °C. *S* – $K_{3+x}Li_{1-x}Mg_4(MoO_4)_6$

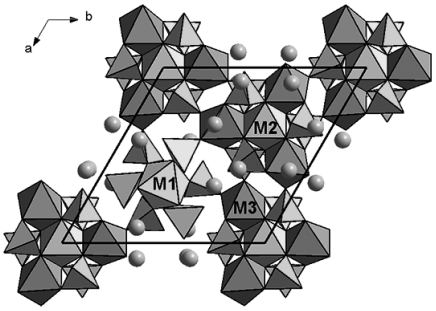

Fig. 8. The projection of the fragment of structure of triple molybdate $K_{3+x}Li_{1-x}A_4(MoO_4)_6$ (*A* = Mg, Mn, Co) on the plane (001).

MoO4 in large extra-framework cavities there are potassium ions. In the systems Na_2MoO_4–K_2MoO_4–$AMoO_4$ (*A* = Ni, Mg, Co) there are formed triple molybdates $K_3NaA_4(MoO_4)_6$ similar in structure [44], figurative points are located on quasi-binary sections of $K_3Na(MoO_4)_2$–$AMoO_4$. In the structures of these compounds the positions M1, M2 and M3 are occupied by the cations Na^+, A^{2+} and A^{2+}, respectively, and the positions of potassium, as in the previous case are occupied only half. The data on these triple molybdates are given in table. 4. The isostructurality of considered triple molybdates to sodium-ion conductor II- $Na_3Fe_2(AsO_4)_3$ gives reason to expect the presence of increased ionic conductivity. It is assumed that the ways of transport of ions in these phases are similar to found in the structure of II- $Na_3Fe_2(AsO_4)_3$, where Na^+ cations are moved through the defective positions of sodium with CN = 9 and octahedral site M1, in the neighbouring coordination polyhedra and form three-dimensional network.

In the systems Li_2MoO_4–Rb_2MoO_4–$AMoO_4$ (*A* = Mg, Mn, Co, Ni) and Li_2MoO_4–Cs_2MoO_4–$AMoO_4$ (*A* = Mg, Mn, Ni) triple molybdates aren't formed. In systems with Rb and Zn (Fig. 9, a) and cesium-containing systems with Co and Zn (Fig. 9, *b*) $Rb_3LiZn_2(MoO_4)_4$ и $Cs_3LiA_2(MoO_4)_4$ (*A* = Co, Zn) are found [41-43], the isostructural cubic $Cs_6Zn_5(MoO_4)_8$ [23, 24]. The uniqueness of the composition and structure $Cs_6Zn_5(MoO_4)_8$ is connected with the incompleteness of the tetrahedral positions of the zinc, where the sixth part is vacant. The filling of vacancies by ions Li^+ and other singly charged cations M^+ according to scheme $Zn^{2+} + \square \rightarrow 2M^+$ creates the conditions for the synthesis of new compounds. An introduction to the structure of cubic $Cs_6Zn_5(MoO_4)_8$ of singly charged cations M^+ = Na, Ag with close to Zn^{2+} ionic radius obtained cubic phases $Cs_3MZn_2(MoO_4)_4$ with disordered distribution of cations M^+ on the positions of the Zn^{2+}. The features $Cs_3MZn_2(MoO_4)_4$ (*M* = Na, Ag) are given in table. 4. According to our data [43, 50], between $Cs_3MZn_2(MoO_4)_4$ (*M* = Li, Na) and $Cs_6Zn_5(MoO_4)_8$ there are continuous solid solutions (Fig. 9, *b*) with the gradual filling of the cationic vacancies in the

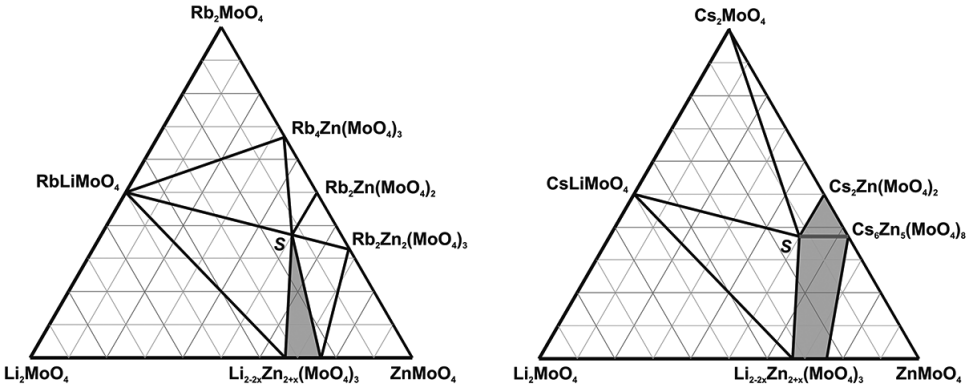

Fig. 9. Subsolidus triangulation of the triple systems at 510 °C: *a* – Li_2MoO_4–Rb_2MoO_4–$ZnMoO_4$; *b* – Li_2MoO_4–Cs_2MoO_4–$ZnMoO_4$. *S* – $M_3LiZn_2(MoO_4)_4$ (*M* = Rb, Cs)

structure $Cs_6Zn_5(MoO_4)_8$. It is likely that a similar phenomenon occurs in the case of $Cs_3AgZn_2(MoO_4)_4$. The formation of such solid solutions gives the opportunity within certain limits to control the composition, stability and properties of phases on the basis of $Cs_6Zn_5(MoO_4)_8$.

It should be noted that the substitution and the simultaneous introduction into the position of zinc in the structure $Cs_6Zn_5(MoO_4)_8$ different valent cations with very different ionic radius on the scheme $5Zn^{2+} + \square \rightarrow 2R^{3+} + 4Li^+$ leads to the formation of the group of triple molybdates $Li_2M_3R(MoO_4)_4$ (*MR* = CsFe, CsGa, RbGa, CsAl, RbAl, TlAl) described above. In the latter case, the cations Li^+ and R^{3+} are distributed orderly in structure, which leads to a tetragonal distortion of the structure of the prototype.

The basis of the structures of the triple molybdates of both series, as structures $Cs_6Zn_5(MoO_4)_8$ are delicate three-dimensional frames. In phases with divalent metals they are formed by tetrahedrons of two sorts – around the molybdenum

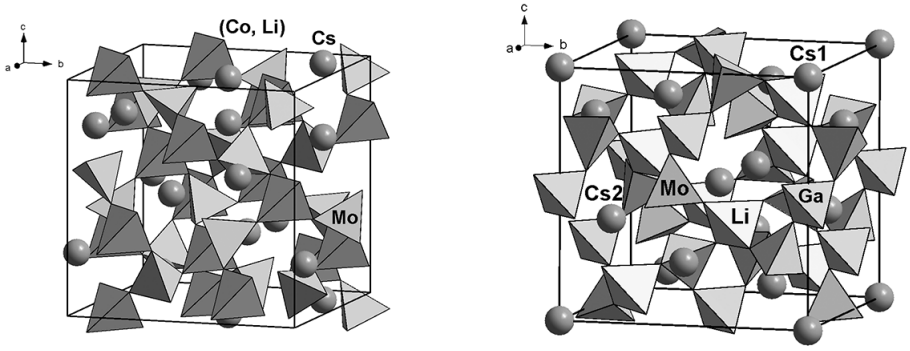

Fig. 10. The structure of triple molybdates derived from patterns $Cs_6Zn_5(MoO_4)_8$ [23, 24]: *a* – структура $LiCs_3Co_2(MoO_4)_4$ (pr. gr. $I\bar{4}3d$) [41]; *b* – структура $Li_2Cs_3Ga(MoO_4)_4$ (pr. gr. $I\bar{4}2d$) [42]

and "mixed" position of lithium (sodium, silver) and a divalent cation; in the compounds with trivalent metals - tetrahedra MoO_4, LiO_4 and RO_4. In large voids of the framework there are large singly charged cations with CN = 12 (Fig. 10).

All phases of family $Cs_6Zn_5(MoO_4)_8$ have acentric structure and perspective to create materials for nonlinear optics. Moreover, an open frame structure leads to the manifestation of these compounds ion-conductive properties. The most significant results were obtained for $Rb_3LiZn_2(MoO_4)_4$ and $Tl_3Li_2Al(MoO_4)_4$, the values of ionic conductivity (of the order of $2{\cdot}10^{-2}$ Sm/sm at 520 and 350 °C, respectively), bring them closer to superionic conductors.

In the systems Li_2MoO_4–M_2MoO_4–$AMoO_4$ (M = Na, K, Rb, Cs; A = Ca, Sr, Pb, Ba, Cd) triple molybdates aren't formed, however, there are areas of solid solutions (up to 15 mol. %) on the basis of double molybdates from faceting systems M_2MoO_4–$AMoO_4$ [51].

In the study of solution-melt crystallization (solvent – $Cs_2Mo_2O_7$) in the systems Na_2MoO_4–Cs_2MoO_4–$AMoO_4$ (A = Ni, Co, Mn) the crystals $CsNa_5M_3(MoO_4)_6$ [47] related to the type alluaudite were isolated and structurally were investigated. The oxygen octahedra around the cations A^{2+} and Na^+ are connected with common edges and faces, and then by common vertices with the MoO_4 tetrahedra into a three-dimensional frame, which is parallel (100) is divided into two kinds of layers (Fig. 11). In one of these layers (Fig. 11) the wide channels filled with cesium ions pass parallel to the axis c, which occupy half their positions and have CN = 8. The comparison of eludicating structures $CsNa_5A_3(MoO_4)_6$ and $Na_{4-2x}A_{1+x}(MoO_4)_3$ (A = Ni, Co, Mn) shows that in the triple molybdates part of the cations Na^+ in the channels was replaced with Cs^+, significantly increased the parameters of the cell along the axis a and accordingly the width of the channels were significantly increased. View as along these channels the transport of sodium ions may be, it may increase the ionic conductivity. The close relationship of phases $CsNa_5A_3(MoO_4)_6$ and $Na_{4-2x}A_{1+x}(MoO_4)_3$ (A = Ni, Co, Mn) can indicate the formation of solid solutions between them, which requires additional researches. The features $CsNa_5A_3(MoO_4)_6$ (A = Ni, Co, Mn) are given in table. 4.

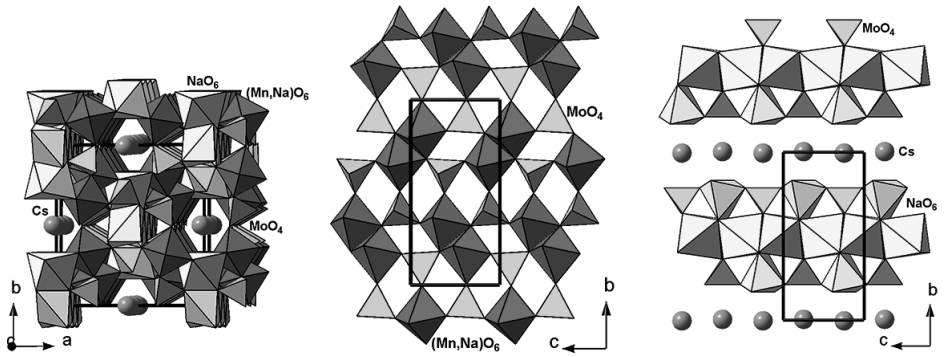

Fig. 11. Structure $CsNa_5Mn_3(MoO_4)_6$:
a – general view; *b,c* - two types of layers of polyhedra projected on (100)

In the systems Na_2MoO_4–Cs_2MoO_4–$AMoO_4$ (A = Co, Mn) also highlighted the triple molybdates of composition $Cs_4Na_{10}A_5(MoO_4)_{12}$ [46, 48] (Fig. 12, table 4) also were highlighted, which were very similar in structure to the above compounds $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = In, Sc, Fe), forming together with them obviously the single family of phases with similar metrics of cells and different symmetry. The structure $Cs_4Na_{10}Co_5(MoO_4)_{12}$ (pr. gr. *Pbca*) is most symmetrical, which can be regarded as the ancestor of this family. The symmetry the other compounds may be raised at phase transitions, which must be accompanied by disordering of the structure and the possible increase in the mobility of sodium cations.

In this regard, we can expect high ionic conductivity at triple molybdates

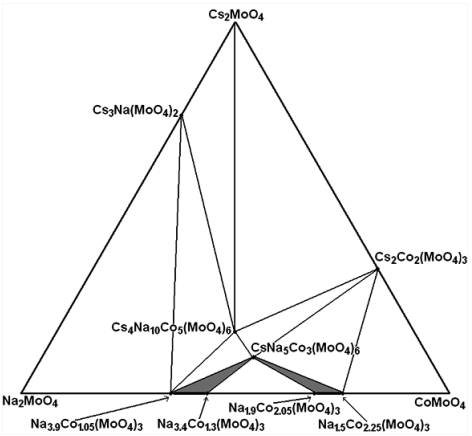

Fig. 12. Subsolidus triangulation of the Na_2MoO_4–Cs_2MoO_4–$CoMoO_4$ at 480 °C

$Cs_4Na_{10}A_5(MoO_4)_{12}$ (A = Co, Mn, as this is the case for $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = In, Sc, Fe).

Concluding remarks

Our carried studies of triple molybdates of the type 1-1-2 and 1-1-3 show that among them there are several families of isostructural or closely related in structure phases. The systems with trivalent metals have higher phase-forming ability, the large stoichiometric and structural diversity in which the triple molybdates belonging to 14 structural types (families) form, whereas triple molybdates of the type 1-1-2 belong only to four isostructural series. One from these explanations for this may be the wider range of cations R^{3+} and their sizes compared to the ions A^{2+} in the phase-forming systems M'_2MoO_4–M''_2MoO_4–$AMoO_4$ (M' = Li, Na; M'' = K, Rb, Cs; A = Mg, Mn, Co, Ni, Zn). A number of identified families of triple molybdates of types 1-1-3 and 1-1-2 may be promising as functional materials. This is especially true of the family of compounds $LiMR_2(MoO_4)_4$ with interesting spectral-luminescent properties, as well as lithium- and sodium-containing triple molybdates of different structures, which may show an increased ion conductivity. Among the latest the compounds of families $Cs_6Zn_5(MoO_4)_8$, II-$Na_3Fe_2(AsO_4)_3$ and alluaudito-similar phase $Na_{25}Cs_8R_5(MoO_4)_{24}$ (R = In, Sc, Fe) and $Cs_4Na_{10}M_5(MoO_4)_{12}$ (M = Co, Mn) for which the relevant researches have already conducted. From the crystallochemical point of view in this regard the compounds $LiMR_2(MoO_4)_4$ are also interesting, where the ions Li^+ fill internodic voids of structural type $BaNd_2(MoO_4)_4$ and the hexagonal or trigonal phases S_1–S_4 (table. 2, 3), in which the sodium ions have a nonstandard (trigonal-prismatic or lower) coordination that can contribute to ionic conductivity. Nonlinear optical properties

can be expected from acentric triple molybdates $LiK_2In(MoO_4)_3$, $LiCs_4Al(MoO_4)_4$, $Na_5Cs_7Yb_2(MoO_4)_9$, $NaCs_2Bi(MoO_4)_3$ and their analogues, as well as the phases of the family $Cs_6Zn_5(MoO_4)_8$.

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